

# Quantum Confinement Effects in Semiconductor Clusters II

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## Abstract

The band gaps and spectral shifts of CdS, CdSe, CdTe, AlP, GaP, GaAs, and InP semiconductor clusters are calculated from band structure calculations using accurate local and non-local empirical pseudopotentials. The effect of spin-orbit coupling on the band structures is included in the calculations when they are important. The complete set of pseudopotential parameters and full computational details are reported for all these semiconductors. The calculated spectral shifts of zinc-blende and wurtzite CdS, wurtzite CdSe, and zinc-blende InP clusters are in good agreement with experiments over a range of cluster sizes. The effect of crystal structure on the band gaps is small in large clusters but becomes important in small clusters. In the absence of experimental data, our calculations provide reasonable estimates of expected spectral shifts for the other clusters. These results demonstrate that the empirical pseudopotential method yields unique insights into the quantum confinement effects and is a powerful tool for calculating the spectral shifts of semiconductor clusters.

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## I. INTRODUCTION

Clusters are an embryonic form of matter whose microscopic study provides insights into the evolution of material properties from molecules and surfaces to solids [1–3]. Furthermore, clusters have been shown to exhibit exotic optical properties and reactivities quite different from those in molecules and solids [4–6]. For these reasons, theoretical studies on clusters are critical to the design and synthesis of advanced materials with desired optical, electronic, and chemical properties [7–16]. Such studies are at the interface of the traditional fields of quantum chemistry, solid state chemistry, and statistical mechanics [17–20]. Hence, physicists, chemists, and material scientists are working individually and in teams to unearth the fundamental principles underlying the structure, dynamics, and reactivities of these clusters [21–26]. However, theoretical studies on the spectroscopy of semiconductor clusters have lagged far behind [27].

The interest on the spectroscopy of semiconductor clusters arose from the discovery by Louis Brus that such clusters can be synthesized in colloidal suspensions by controlled liquid phase precipitation reactions [28]. The radii of the clusters thus synthesized are usually in the 5-100 Å range. Furthermore, the X-ray and transmission electron microscopy (TEM) experiments have shown that these clusters have the same lattice structures as the corresponding bulk materials [4,5,17,18,29]. Finally, it is possible to prepare macroscopic samples of these clusters either in powder form or in colloidal suspension form. Such a versatility in sample preparation has made it possible for experimentalists to investigate the physical and optical properties of these clusters in detail [4]. Indeed, very sophisticated experiments are currently underway in various laboratories to understand the absorption spectra of these clusters as a function of the cluster size [5,17–19]. What is remarkable about these clusters is that the electronic spectra of these clusters are not the same as that of the bulk, even though the clusters have the same structural properties as the crystals [4]. The absorption spectra of clusters show relatively sharp resonances superimposed on a continuum. The first absorption peak in the spectrum corresponds to the threshold for the absorption of light by the semiconductor cluster. It corresponds to the exciton energy, the energy needed to excite an electron from the top of the valence to the bottom of the conduction band. Quantitative prediction of the shift of the exciton energy with cluster size had been an outstanding problem for a decade. Simple theoretical calculations based on an effective mass model (EMM) were not successful and *ab initio* quantum chemistry electronic structure calculations are impossible for these clusters consisting of thousands of electrons. Consequently, what was needed was a simple model that captured the essential physics of the problem at hand.

Recently, we developed such a model and solved this problem [30]. We used accurate pseudopotentials to carry out band structure calculations and obtained the electronic energy levels of these clusters. Our calculations of the threshold for the absorption of light by CdS clusters yielded results in excellent agreement with experiment over a range of cluster sizes [30]. Furthermore, we predicted two new effects. First, we found that the exciton energies in small CdS clusters are sensitive to the crystal structure, even though such a sensitivity is absent in large clusters [30]. Second, we found that the vertical Franck-Condon transition energies in indirect gap clusters exhibit an anomalous redshift in small clusters [30]. In sharp contrast, the extant theoretical models always yielded monotonic blueshift of the transition

energies with decreasing cluster size [30].

The band structure model we employ here has also yielded a noteworthy insight into the nature of the electronic transitions in semiconductor clusters. The question is whether the electronic transitions observed in these clusters are related in any way to the bulk transitions. Previous theoretical calculations implicitly assumed that the electronic states in semiconductor clusters are similar to those in molecules and hence they are qualitatively different from those found in bulk. In sharp contrast, our band structure model underlies the presumption that the electronic states in nanoscale clusters are similar to those in bulk. Consequently, we use the bulk language (direct vs. indirect) to classify the electronic transitions in clusters. Recent experiments of Brus and co-workers [29] on the luminescence of Si clusters support our assumption. Based on the analysis of the luminescence of Si clusters, Brus and co-workers concluded that the lowest energy exciton transition is essentially an indirect gap transition, even though the spectrum has blueshifted by almost 0.9 eV [29]. This observation that bulk-like transitions are preserved even in clusters supports our band structure model.

In this paper we extend our band structure calculations to a variety of semiconductor clusters for two reasons: First, we wish to investigate the reliability of our band structure model by repeating these calculations on different systems for which accurate experimental data are now available. Second, the accuracy of our calculations on wurtzite clusters could not be verified previously because of the absence of experimental data on those clusters at that time. Since highly accurate experimental data are now available for wurtzite CdS and CdSe clusters, we felt the need to repeat our band structure calculations on these clusters. In this paper we also give the results of our calculations on CdTe, AlP, GaP, GaAs, and InP clusters. While accurate and reliable experimental data on these clusters are not available at present, we hope that our calculations provide reasonable estimates of the expected spectral shifts as a function of cluster size.

Experimental synthesis of semiconductor clusters is still a challenging problem at present. One major difficulty is establishing a suitable synthetic route that yields nanometer scale clusters. The other major difficulty is determining optimal control parameters that yield clusters with a narrow size distribution. While both these problems remain to be fully solved, significant progress is being made daily. We hope the present paper will serve as a useful guide to the experimentalists on the expected behavior of spectral shifts in a variety of technologically important nanoscale semiconductor clusters.

This paper is organized as follows: Section II gives the empirical pseudopotential theory of band structure calculations, Sec. III presents the band structure model, Sec. IV gives some computational details, and Sec. V presents results of these calculations on a variety of semiconductor clusters. Finally, we summarize this paper in Sec. VI.

## II. EMPIRICAL PSEUDOPOTENTIAL METHOD

The electronic structure calculations of the semiconductor clusters are carried out using the empirical pseudopotential method (EPM) that has been previously used for the investigations of the optical properties of bulk semiconductor materials and clusters [30]. This method consists of solving the Schrödinger equation using an empirically determined pseudopotential for the valence electron,

$$\mathcal{H} = -\frac{\hbar^2}{2m}\nabla^2 + V_p, \quad (1)$$

$$V_p(\mathbf{r}, E) = V_L(\mathbf{r}) + \sum_{l=0}^{\infty} \Pi_l^\dagger A_l(E) f_l(\mathbf{r}) \Pi_l, \quad (2)$$

where the first term  $V_L$  is the purely local part, the second term gives the non-local ( $V_{NL}$ ) part, and  $\Pi_l$  is the projection operator for angular momentum states  $l$ . The local part of the pseudopotential is given by

$$V_L(\mathbf{r}) = \sum_{\mathbf{G}} [V_S(\mathbf{G})S_S(\mathbf{G}) + iV_A(\mathbf{G})S_A(\mathbf{G})] \exp(i\mathbf{G} \cdot \mathbf{r}), \quad (3)$$

where  $V_S$  and  $V_A$  are the symmetric and anti-symmetric form factors, respectively, determined by fitting them to the experimental optical data. Similarly,  $S_S$  and  $S_A$  are the symmetric and anti-symmetric structure factors, respectively, determined from the crystal structure. The function  $A_l(E)$  is the energy dependent well depth

$$A_l(E) = \alpha_l + \beta_l [E^0(K)E^0(K')]^{1/2} - E^0(K_F)], \quad (4)$$

where  $E^0(K) = \hbar^2 K^2 / 2m$  and  $K_F = (6\pi^2 z / \Omega_c)^{1/3}$  is the Fermi wave-vector with  $z$  the number of valence electrons per unit cell and  $\Omega_c$  the volume of the unit cell.  $f_l(\mathbf{r})$  is conveniently taken to be the square well

$$f_l(\mathbf{r}) = \begin{cases} 1 & \mathbf{r} < R_l \\ 0 & \mathbf{r} \geq R_l. \end{cases} \quad (5)$$

$\alpha_l, \beta_l$ , and  $R_l$  are the non-local parameters of the EPM theory to be determined from the experimental optical data.

### A. Non-local Pseudopotentials

In many instances the local part of the pseudopotential ( $V_L$ ) is sufficiently accurate to represent the gross features of the band structures correctly. However, the non-local pseudopotential is much more accurate over a broad range of energy scales. In particular, the calculated band widths and band dispersion are closer to the experimental values with the non-local calculations than with the local calculations. The non-local calculations are also much more satisfactory theoretically since they incorporate the correct angular momentum dependence nature of the pseudopotential experienced by the valence electrons.

The local contribution to the pseudopotential is given by Eq. (3). Evaluation of these matrix elements of the Hamiltonian will be described in Secs. IIC and IID for zinc-blende and wurtzite structures, respectively. In the plane wave basis the matrix elements of the non-local pseudopotential are of the form

$$V_{NL}(\mathbf{K}, \mathbf{K}') = \frac{4\pi}{\Omega_a} \sum_{l,i} A_l^i(E) P_l(\cos(\Theta_{KK'})) S^i(\mathbf{K} - \mathbf{K}') F_l^i(K, K'), \quad (6)$$

as discussed elsewhere [31].

## B. Spin-Orbit Coupling in Band Theory

In light elements the electron spin ( $s$ ) and orbital angular momentum ( $l$ ) are both good quantum numbers, since the magnetic field generated by the orbiting electron is too weak to induce coupling with the electron spin. However, in heavier elements the nearly relativistic speed of the valence electron produces a sufficiently large magnetic field that  $l$  and  $s$  are coupled, giving rise to  $j = l + s$  as the good quantum number. The spin-orbit interaction thus couples electron dynamics in spin and ordinary spaces, thereby reducing the overall symmetry of the Hamiltonian. This relativistic effect is represented by the operator [32]

$$H_{SO} = \frac{\hbar}{4m^2c^2} \sigma \cdot (\nabla V_p \times p), \quad (7)$$

where  $\sigma$  are the Pauli spin matrices,  $V_p$  is the pseudopotential,  $p$  is the electron momentum,  $m$  is the true electron mass, and  $c$  is the speed of light. The matrix elements of the new Hamiltonian in the plane wave representation are given by [33]

$$\begin{aligned} \langle \mathbf{k} + \mathbf{G}', s' | \mathbf{H} | \mathbf{k} + \mathbf{G}, s \rangle &= \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G}\mathbf{G}'} \delta_{ss'} \\ &+ S_S(\mathbf{G} - \mathbf{G}') [V_S(|\mathbf{G} - \mathbf{G}'|^2) \delta_{ss'} - i\lambda_S(\mathbf{G}' \times \mathbf{G}) \cdot \sigma_{ss'}] \\ &+ iS_A(\mathbf{G} - \mathbf{G}') [V_A(|\mathbf{G} - \mathbf{G}'|^2) \delta_{ss'} - i\lambda_A(\mathbf{G}' \times \mathbf{G}) \cdot \sigma_{ss'}]. \end{aligned} \quad (8)$$

For a binary semiconductor consisting of two types of atoms ( $A \neq B$ ), we define

$$\lambda_S = \frac{1}{2}(\lambda_1 + \lambda_2), \quad \lambda_A = \frac{1}{2}(\lambda_1 - \lambda_2), \quad (9)$$

where

$$\lambda_1 = \mu B_{nl}^A(G) B_{nl}^A(G'), \quad \lambda_2 = \alpha \mu B_{nl}^B(G) B_{nl}^B(G'), \quad (10)$$

$\mu$  is the adjustable parameter chosen in order to obtain the splitting  $\Delta$  of the valence band at  $\Gamma$  correctly, and  $\alpha$  is the ratio of the contribution from atom A to the contribution from atom B at  $\Gamma$ . The  $B_{nl}$  are defined as

$$B_{nl}(G) = C \int_0^\infty r^2 R_{nl}(r) j_l(Gr) dr, \quad (11)$$

where  $j_l$  are the spherical Bessel functions,  $C$  is determined by the condition

$$\lim_{G \rightarrow 0} \frac{B_{nl}(G)}{G} = 1, \quad (12)$$

and  $R_{nl}$  are the radial parts of the outermost electron wave functions taken from the Herman-Skillman tables [34]. For simplicity we always used a value of  $\alpha = 1.0$  and  $C = 1.0$ .

The band structures of semiconductors have several common features: At  $\Gamma$  the HOMO is split by the spin-orbit coupling [35]. Specifically, counting the spin, for the zinc-blende structure the HOMO band is sixfold degenerate. The spin-orbit interaction splits this band into an upper fourfold degenerate  $\Gamma_8$  component, and a lower twofold degenerate  $\Gamma_7$  component. The conduction band  $\Gamma_1$  is twofold degenerate [36]. For the wurtzite structure, the degeneracy of the  $\Gamma$  band is already removed by the crystal field, leading to an upper twofold

degenerate band, and a lower fourfold degenerate band. The spin-orbit coupling then splits the lower band into two twofold degenerate bands [36]. For both systems, wurtzite and zinc-blende, the highest three valence bands are called heavy-mass, light-mass, and split-off band, respectively [36]. Transitions between these three valence bands to the conduction band are traditionally labelled A, B, and C [37]. The atomic orbital approach is especially useful for describing valence bands near  $\Gamma$ . From this perspective, the HOMO bands arise from the valence  $p$  orbitals while the LUMO band arises from the  $s$  orbitals [36]. In polar semiconductors such as CdS and CdSe, HOMO bands originate primarily from the anion, and LUMO bands from the cation. However, in non-polar semiconductors such as CdTe and GaAs, considerable mixing of the cation and anion orbitals will take place. Since our interest is in reproducing the splitting of the valence  $p$  bands near HOMO, our calculations considered only the contributions from the outermost  $p$  orbitals. We do not consider spin-orbit effects on the innercore or the  $d$ -electron states since these states are eliminated in EPM through the use of the pseudopotential. The  $s$  orbitals do not exhibit spin-orbit splitting since their orbital angular momentum is zero.

### C. Local Pseudopotentials of Zinc-blende Structure Crystals

The local pseudopotential ( $V_L$ ) experienced by a valence electron at a point  $\mathbf{r}$  inside a crystal lattice is given by

$$V_L(\mathbf{r}) = \sum_{\mathbf{R},j} v_j(\mathbf{r} - \mathbf{R} - \mathbf{d}_j), \quad (13)$$

where the summation is over all the basis atoms  $j$  at each lattice point  $\mathbf{R}$ , and  $v_j$  is the atomic pseudopotential due to the  $j$ th basis atom at the lattice site  $\mathbf{R}$ . Fourier expansion of  $v_j$  yields,

$$V_L(\mathbf{r}) = \frac{1}{Nn_a} \sum_{\mathbf{G}} \sum_{\mathbf{R},j} v_j(\mathbf{G}) \exp[i\mathbf{G} \cdot (\mathbf{r} - \mathbf{R} - \mathbf{d}_j)], \quad (14)$$

where  $N$  are the number of unit cells and  $n_a$  are the number of basis atoms per unit cell.

The zinc-blende (or sphalerite) lattice consists of two interpenetrating fcc lattices, displaced from each other along the body diagonal by  $a_0/4$ ,  $a_0$  being the lattice constant of the unit cell. Consequently, we may view the zinc-blende structure as an fcc lattice with two different  $A \neq B$  basis atoms per unit cell. For this case,  $n_a = 2$ ,  $v_1(\mathbf{G}) \neq v_2(\mathbf{G})$ , and  $\mathbf{d}_1 = -\mathbf{d}_2 = -\mathbf{t}_1 = -(1, 1, 1)/8$ . Explicitly summing the above equation now yields,

$$V_L(\mathbf{r}) = \sum_{\mathbf{G}} \left[ \frac{1}{n_a} \sum_j v_j(\mathbf{G}) \exp(-i\mathbf{G} \cdot \mathbf{d}_j) \right] \exp(i\mathbf{G} \cdot \mathbf{r}) \quad (15)$$

$$= \sum_{\mathbf{G}} \left\{ \frac{1}{2} [v_1(\mathbf{G}) \exp(i\mathbf{G} \cdot \mathbf{t}_1) + v_2(\mathbf{G}) \exp(-i\mathbf{G} \cdot \mathbf{t}_1)] \right\} \exp(i\mathbf{G} \cdot \mathbf{r}) \quad (16)$$

$$= \sum_{\mathbf{G}} [V_S(\mathbf{G})S_S(\mathbf{G}) + iV_A(\mathbf{G})S_A(\mathbf{G})] \exp(i\mathbf{G} \cdot \mathbf{r}), \quad (17)$$

where

$$V_S(\mathbf{G}) = \frac{1}{2} [v_1(\mathbf{G}) + v_2(\mathbf{G})], \quad V_A(\mathbf{G}) = \frac{1}{2} [v_1(\mathbf{G}) - v_2(\mathbf{G})] \quad (18)$$

are the symmetric ( $V_S$ ) and anti-symmetric ( $V_A$ ) form factors and

$$S_S(\mathbf{G}) = \cos(\mathbf{G} \cdot \mathbf{t}_1), \quad S_A(\mathbf{G}) = \sin(\mathbf{G} \cdot \mathbf{t}_1) \quad (19)$$

are the symmetric ( $S_S$ ) and anti-symmetric ( $S_A$ ) structure factors, respectively. Defining the reciprocal lattice vectors  $\mathbf{G}$  as

$$\mathbf{G} = \frac{2\pi}{a_0} (G_x, G_y, G_z) \quad (20)$$

we obtain

$$S_S(\mathbf{G}) = \cos \left[ \frac{\pi}{4} (G_x + G_y + G_z) \right], \quad S_A(\mathbf{G}) = \sin \left[ \frac{\pi}{4} (G_x + G_y + G_z) \right]. \quad (21)$$

If we now specialize to the case of  $A = B$ , we obtain the local pseudopotential for diamond structure:

$$V_L(\mathbf{r}) = \sum_{\mathbf{G}} V_S(\mathbf{G}) S_S(\mathbf{G}) \exp(i\mathbf{G} \cdot \mathbf{r}). \quad (22)$$

#### D. Local Pseudopotentials of Wurtzite Structure Crystals

The wurtzite crystals are made of two interpenetrating hexagonal close packed (hcp) lattices. One hcp lattice is entirely made of A type atoms and the other entirely of B type atoms ( $A \neq B$ ) and these two lattices are displaced from each other by  $2t_2 = \frac{3}{8}c_0$  along the c-axis. However, the hcp lattice is not a Bravais lattice. The hcp lattice consists of two interpenetrating simple hexagonal Bravais lattices, displaced from one another by  $2t_1 = (\frac{1}{3}\mathbf{a}_1, \frac{1}{3}\mathbf{a}_2, \frac{1}{2}\mathbf{a}_3)$ , where  $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$  are the direct lattice primitive translation vectors of the simple hexagonal Bravais lattice. Hence, the wurtzite structure is a network of four simple hexagonal lattices, with four atoms per unit cell and two different types of atoms. For this case  $n_a = 4$  and the position vectors of the four basis atoms in the unit cell are given by

$$\mathbf{d}_1 = -(\mathbf{t}_1 + \mathbf{t}_2) \quad (23)$$

$$\mathbf{d}_2 = -(\mathbf{t}_1 - \mathbf{t}_2) \quad (24)$$

$$\mathbf{d}_3 = (\mathbf{t}_1 + \mathbf{t}_2) \quad (25)$$

$$\mathbf{d}_4 = (\mathbf{t}_1 - \mathbf{t}_2). \quad (26)$$

The local pseudopotential of the valence electron interacting with a periodic wurtzite lattice is given by

$$V_L(\mathbf{r}) = \sum_{\mathbf{G}} \left[ \frac{1}{n_a} \sum_j v_j(\mathbf{G}) \exp(-i\mathbf{G} \cdot \mathbf{d}_j) \right] \exp(i\mathbf{G} \cdot \mathbf{r}) \quad (27)$$

$$= \sum_{\mathbf{G}} \frac{1}{n_a} \{ v_1(\mathbf{G}) [\exp(-i\mathbf{G} \cdot \mathbf{d}_1) + \exp(-i\mathbf{G} \cdot \mathbf{d}_4)] \\ + v_2(\mathbf{G}) [\exp(-i\mathbf{G} \cdot \mathbf{d}_2) + \exp(-i\mathbf{G} \cdot \mathbf{d}_3)] \} \exp(i\mathbf{G} \cdot \mathbf{r}), \quad (28)$$

since atoms 1 and 4, and 2 and 3 are identical in the wurzite lattice. Rewriting  $v_1$  and  $v_2$  in terms of  $V_S$  and  $V_A$  from Eq. (18) we obtain

$$V_L(\mathbf{r}) = \sum_{\mathbf{G}} [V_S(\mathbf{G})S_S(\mathbf{G}) + iV_A(\mathbf{G})S_A(\mathbf{G})] \exp(i\mathbf{G} \cdot \mathbf{r}), \quad (29)$$

where the symmetric ( $S_S$ ) and anti-symmetric ( $S_A$ ) structure factors are given by

$$S_S(\mathbf{G}) = \frac{1}{n_a} \sum_j \exp(-i\mathbf{G} \cdot \mathbf{d}_j), \quad S_A(\mathbf{G}) = \frac{-i}{n_a} \sum_j P_j \exp(-i\mathbf{G} \cdot \mathbf{d}_j), \quad (30)$$

where  $P_j = +1$  when  $j = 1, 4$  and  $P_j = -1$  when  $j = 2, 3$ . Thus the pseudopotentials of wurzite and zinc-blende crystals differ from each other only in the definition of the structure factors. We can carry out the summations in Eq. (30) as follows.

The hexagonal lattice is characterized by three parameters:  $a_0$ ,  $c_0$ , and  $u_0$ . Like zinc-blende, wurzite lattice has tetrahedral coordination about each ion, but the orientation of the tetrahedron is different from that of zinc-blende. If we assume perfect tetrahedral coordination, then

$$\frac{c_0}{a_0} = \sqrt{\frac{8}{3}}, \quad u_0 = 0.375 = \frac{3}{8}. \quad (31)$$

The direct lattice primitive translation vectors of the simple hexagonal Bravais lattice are [38]

$$\mathbf{a}_1 = (1, 0, 0)a_0, \quad \mathbf{a}_2 = \left(\frac{1}{2}, \frac{\sqrt{3}}{2}, 0\right)a_0, \quad \mathbf{a}_3 = \left(0, 0, \frac{c_0}{a_0}\right)a_0. \quad (32)$$

With this definition, the position vectors of the basis atoms are

$$\mathbf{d}_1 = -\frac{1}{4} \left[ 1, \frac{1}{\sqrt{3}}, (1 + 2u_0)\frac{c_0}{a_0} \right] a_0 \quad (33)$$

$$\mathbf{d}_2 = -\frac{1}{4} \left[ 1, \frac{1}{\sqrt{3}}, (1 - 2u_0)\frac{c_0}{a_0} \right] a_0 \quad (34)$$

$$\mathbf{d}_3 = \frac{1}{4} \left[ 1, \frac{1}{\sqrt{3}}, (1 + 2u_0)\frac{c_0}{a_0} \right] a_0 \quad (35)$$

$$\mathbf{d}_4 = \frac{1}{4} \left[ 1, \frac{1}{\sqrt{3}}, (1 - 2u_0)\frac{c_0}{a_0} \right] a_0 \quad (36)$$

in cartesian coordinate representation.

In the zinc-blende crystal the nearest neighbor atoms are located half-way along the face diagonal of the fcc lattice. Consequently, if  $a_0(\text{zb})$  is the lattice constant of the zinc-blende crystal, then the nearest neighbor distance is

$$r_n(\text{zb}) = \frac{1}{\sqrt{2}}a_0(\text{zb}). \quad (37)$$

In the hexagonal crystal, the nearest neighbor atoms are located along the edges of the hexagon. Consequently,



$$r_n(\text{hex}) = a_0(\text{hex}) \quad (38)$$

Since  $r_n(\text{zb}) = r_n(\text{hex})$ , comparing Eqs. (37) and (38) we obtain the relation

$$a_0(\text{zb}) = \sqrt{2}a_0(\text{hex}). \quad (39)$$

and

$$\mathbf{G} = \frac{\sqrt{2}\pi}{a_0(\text{hex})}(G_x, G_y, G_z). \quad (40)$$

This definition allows the comparison of  $\mathbf{G}$  vectors of zinc-blende and wurtzite crystals on an equal footing.

Substituting Eqs. (23-26) into (30) and carrying out some algebraic manipulations we obtain

$$S_S(\mathbf{G}) = \cos(\mathbf{G} \cdot \mathbf{t}_1) \cos(\mathbf{G} \cdot \mathbf{t}_2), \quad S_A(\mathbf{G}) = -\cos(\mathbf{G} \cdot \mathbf{t}_1) \sin(\mathbf{G} \cdot \mathbf{t}_2), \quad (41)$$

where

$$\mathbf{t}_1 = \frac{1}{6}(\mathbf{a}_1 + \mathbf{a}_2) + \frac{\mathbf{a}_3}{4} = \left(\frac{1}{4}, \frac{1}{\sqrt{48}}, \frac{1}{\sqrt{6}}\right)a_0, \quad (42)$$

$$\mathbf{t}_2 = \frac{1}{2}u_0\mathbf{a}_3 = (0, 0, \sqrt{u_0}/2)a_0. \quad (43)$$

Finally, substituting Eq. (40) into (41) we obtain

$$S_S(\mathbf{G}) = \cos \left[ \sqrt{2}\pi \left( \frac{G_x}{4} + \frac{G_y}{\sqrt{48}} + \frac{G_z}{\sqrt{6}} \right) \right] \cos(\sqrt{2}\pi G_z \sqrt{u_0}/2), \quad (44)$$

$$S_A(\mathbf{G}) = -\cos \left[ \sqrt{2}\pi \left( \frac{G_x}{4} + \frac{G_y}{\sqrt{48}} + \frac{G_z}{\sqrt{6}} \right) \right] \sin(\sqrt{2}\pi G_z \sqrt{u_0}/2). \quad (45)$$

We can also define  $\mathbf{G}$  as

$$\mathbf{G} = (l\mathbf{b}_1, m\mathbf{b}_2, n\mathbf{b}_3), \quad (46)$$

where  $\mathbf{b}_1, \mathbf{b}_2$ , and  $\mathbf{b}_3$  are the reciprocal lattice primitive translational vectors given by

$$\mathbf{b}_1 = \frac{\sqrt{2}\pi}{a_0}(\sqrt{2}, -\sqrt{\frac{2}{3}}, 0), \quad \mathbf{b}_2 = \frac{\sqrt{2}\pi}{a_0}(0, \sqrt{\frac{8}{3}}, 0), \quad \mathbf{b}_3 = \frac{\sqrt{2}\pi}{a_0}(0, 0, \frac{\sqrt{2}a_0}{c_0}). \quad (47)$$

Substituting Eqs. (47) and (46) into (30), utilizing the relations

$$\mathbf{b}_i \cdot \mathbf{a}_i = 2\pi, \quad \mathbf{b}_i \cdot \mathbf{a}_j = 0 \quad (i \neq j), \quad (48)$$

and carrying out some algebraic manipulations, we obtain

$$S_S(\mathbf{G}) = \cos \left[ 2\pi \left( \frac{l}{6} + \frac{m}{6} + \frac{n}{4} \right) \right] \cos(n\pi u_0), \quad S_A(\mathbf{G}) = \cos \left[ 2\pi \left( \frac{l}{6} + \frac{m}{6} + \frac{n}{4} \right) \right] \sin(n\pi u_0). \quad (49)$$

Eqs. (44)–(45) and (49) are equivalent. We find that the above structure factors yield band structures in excellent agreement with those of Cohen and Bergstresser for wurtzite crystals [39]. We tested our program with both these structure factors and verified that they give identical band structures.

Previously we used a different coordinate system for the definition of the direct lattice vectors of the simple hexagonal Bravais lattice. That definition resulted in structure factors different from the ones given above. While these two definitions are equivalent in principle, in practice the values of the parameters  $V_S$  and  $V_A$  are intimately linked to the choice of the coordinate system and the structure factors determined therefrom. The present choice of the coordinate system that gives rise to the structure factors in Eqs. (44)–(45) and (49) yield correct band structures, in complete agreement with the original band structures of Cohen and Bergstresser [39].

### III. BAND STRUCTURE MODEL

The virtue of EPM is that it reproduces the bulk band structure to better than 0.1 eV accuracy [30]. Other methods are less accurate, especially for the calculations of the band gaps. For example, the calculations based on the density functional theory (DFT) typically underestimate the band gaps by about 30-50%. The DFT based methods optimize the orbitals of the occupied electronic states only, not those of the unoccupied orbitals. This problem remains even when non-local density gradient corrections and other higher-order improvements to the DFT methodology are made. Consequently, the band gaps determined by DFT are in general grossly in error. Furthermore, the DFT calculations are computationally far more expensive compared to EPM. Hence, EPM is suitable for the investigation of the electronic structures of semiconductor clusters.

To apply EPM to the electronic structure calculations of the semiconductor clusters we assume that these clusters have the crystal structure of the bulk semiconductor. This assumption is justified because we are considering relatively large clusters containing tens to hundreds of atoms. Furthermore, the X-ray and TEM experiments on Si, CdS, CdSe, CdTe, GaAs, and InP clusters have shown that the bulk lattice structure is preserved even when the cluster radii are as small as  $\mathbf{R} = 7 \text{ \AA}$  [4,5,17–19,25]. The reason for the preservation of the bulk lattice structure in such small clusters may be due to the presence of ligands on the surfaces of these clusters. These ligands are necessary to prevent the clusters from coalescing into larger units. These ligands also terminate the dangling bonds on the surfaces of these clusters, and thus inhibit structural reconstruction. For this reason, even small clusters seem to possess bulk lattice structure. The major effect of size on cluster structures seems to be small contractions of the bonds relative to their bulk bond lengths.

The band structure calculations are carried out for these clusters in almost the same way as we had done previously for CdS [30]. In bulk semiconductors the allowed wave vectors  $\mathbf{k}$  of the electronic states are continuous. On the other hand, only discrete  $\mathbf{k}$ -states are allowed in clusters. If we model the cluster as a rectangular box with dimensions

$L_x, L_y$ , and  $L_z$ , then a reasonable approximation is to use the bulk pseudopotential  $V_p(\mathbf{r})$  inside the cluster and terminate this potential at the surfaces of the cluster by an infinite potential. The wave vectors of the lowest allowed states are then given by the quantization condition  $\sin(k_x L_x) \sin(k_y L_y) \sin(k_z L_z) = 0$ , whose solution is

$$\mathbf{k} = \pi \left( \frac{n_x}{L_x}, \frac{n_y}{L_y}, \frac{n_z}{L_z} \right), \quad (50)$$

where  $n_x, n_y$ , and  $n_z$  are the quantum numbers of a particle in a box with infinite potentials at the boundaries. The surface ligands act as potential barriers to the valence electrons. Consequently, for low energy excitations under consideration, the assumption of infinite potentials at the boundaries is a good approximation. The energy levels at these allowed  $\mathbf{k}$ -states constitute the band structure of a rectangular box.

Similarly, if we model the cluster as a spherical object of radius  $R$ , the energy levels of the valence electrons will be quantized because of the spherical boundary. The wave vectors of the lowest allowed states are given by  $j_0(k_n R) = 0$ , whose solution is  $\mathbf{k}_n = n\pi/R$  [40]. Since  $\mathbf{k}_n$  is along the radial direction, we project it onto each of the cartesian axes with equal magnitude to obtain cartesian components of  $\mathbf{k}$ . This procedure yields

$$\mathbf{k} = \frac{\pi}{\sqrt{3}R} (n_x, n_y, n_z). \quad (51)$$

for spherical clusters. Sometimes we also model spherical clusters as cubic boxes with  $L = 2R$  as the sidelength of the cube. The energy levels at these allowed  $\mathbf{k}$ -states constitute the band structure of a spherical cluster.

The exciton energy of a cluster of radius  $R$  is given by [30]

$$E_x = E_g - \frac{1.786}{\epsilon R} - 0.248 E_{Ry}, \quad (52)$$

where  $E_g$  is the band gap,  $\epsilon$  is the dielectric constant,  $E_{Ry} = \mu e^4 / 2\epsilon^2 \hbar^2$  is the effective Rydberg energy of the exciton, and  $\mu$  is the reduced mass of the electron-hole pair.

EPM has been shown to reproduce the band gaps to within 0.1 eV for both bulk materials and clusters [30]. Specifically, our predicted indirect band gap of 0.43 eV for a 10 Å radius silicon cluster was found to be in good agreement with recent experimental value of 0.5 eV obtained by Louis Brus and co-workers [41]. Likewise, EPM yielded excellent results for CdS clusters in comparison with experiment [30]. Full details on the computational methodology are given in Refs. [30]. The utility of the proposed method for the calculations of the spectral shifts is also documented in the previous publications [30].

#### IV. COMPUTATIONAL DETAILS

The binary semiconductors being considered in this study all consist of either zinc-blende or wurtzite lattices. Consequently, the Hamiltonian matrices are of complex valued Hermitian matrices. We diagonalized these matrices using the EISPACK routines CH, HTRIDI, and TQLRAT. Typically, we use 283 plane waves to converge the energies to better than 0.01 eV accuracy.

Table I lists the parameters of the local pseudopotentials of zinc-blende and wurtzite CdS and CdSe clusters, while Tables II and III list the corresponding parameters for the non-local pseudopotentials of zinc-blende CdTe, AlP, GaP, GaAs, and InP clusters. Spin-orbit interaction was included in the calculations of wurtzite CdS, wurtzite CdSe, zinc-blende CdTe, and InP clusters. We have verified that the spin-orbit effects are small in AlP, GaP, and GaAs crystals. Consequently, our calculations on these clusters omitted the spin-orbit interaction in the Hamiltonian.

The  $s$  orbitals don't exhibit spin-orbit interaction since they have  $l = 0$  orbital angular momentum. The innercore and  $d$  electron states are eliminated in EPM through the use of the pseudopotentials. Consequently, only the outermost  $p$  orbitals are affected by the spin-orbit interaction. Hence, we used the radial Hartree-Fock-Slater orbitals  $4p$  for Cadmium,  $5p$  for Indium,  $3p$  for Sulphur,  $4p$  for Selenium,  $5p$  for Tellurium, and  $3p$  for Phosphorus in our calculations employing spin-orbit interaction in the Hamiltonian. Other calculations reported in the literature seem to include innercore  $p$  orbital wave functions in the Hamiltonian, instead of the outermost  $p$  orbitals we employ. However, we have verified that in each case we obtain better band structures with the outermost  $p$  orbital wave functions than with the innercore  $p$  orbitals.

We use the standard notation to represent the high symmetry points in the Brillouin zone [30]. For zinc-blende crystals

$$X = (1, 0, 0), W = (1, 0.5, 0), L = (0.5, 0.5, 0.5), \Gamma = (0, 0, 0), U = K = (0, 0.75, 0.75) \quad (53)$$

in units of  $2\pi/a_0$ . For wurtzite crystals, the high symmetry points are defined as

$$\begin{aligned} \Gamma &= (0, 0, 0), K = (\sqrt{2}/3, \sqrt{2}/3, 0), M = (\sqrt{2}/3, 0, 0), \\ A &= (0, 0, a_0)/\sqrt{2}c_0 = (0, 0, \sqrt{3}/4), \\ H &= (\sqrt{2}/3, \sqrt{2}/3, a_0/\sqrt{2}c_0) = (\sqrt{2}/3, \sqrt{2}/3, \sqrt{3}/4), \\ L &= (\sqrt{2}/3, 0, a_0/\sqrt{2}c_0) = (\sqrt{2}/3, 0, \sqrt{3}/4) \end{aligned} \quad (54)$$

in units of  $\sqrt{2}\pi/a_0$ . We map bands along these symmetry points to obtain the complete band structure.

## V. RESULTS AND DISCUSSION

### A. CdS and CdSe Clusters

The CdS and CdSe crystals exist in both zinc-blende and wurtzite form, with the wurtzite form being the ground state structure. In principle it is possible to synthesize clusters also in both these lattice forms. However, the CdS clusters seem to prefer zinc-blende over wurtzite, while CdSe clusters seem to prefer wurtzite over zinc-blende structure. The possibility of being able to synthesize both these isomeric forms of CdS and CdSe clusters, provides an opportunity to investigate the effect of lattice structure on the exciton energies as a function of cluster size.

We use the lattice constant  $a_0 = 5.82 \text{ \AA}$  for zinc-blende and  $a_0 = 4.14 \text{ \AA}$  for wurtzite CdS crystals. Our calculated band gaps are 2.44 eV and 2.52 eV for bulk zinc-blende and

wurtzite CdS, respectively. The experimental result is 2.50 eV [42] for both these structures. We use the lattice constant  $a_0 = 6.08 \text{ \AA}$  for zinc-blende and  $a_0 = 4.30 \text{ \AA}$  for wurtzite CdSe crystals. The calculated band gaps for CdSe are 1.92 eV and 1.79 eV for bulk zinc-blende and wurtzite CdSe, respectively. The experimental values for bulk wurtzite CdSe are 1.75 and 1.83 eV at 80 and 293 K, respectively. We take the average of these two values, 1.79 eV, as the experimental value for both zinc-blende and wurtzite CdSe crystals. According to Cohen and Bergstresser [39] the splitting in energy of the fundamental gap without spin-orbit coupling ( $\Gamma_6^v \rightarrow \Gamma_1^c$ ) is  $E_a + \frac{1}{3}\Delta$ , where  $E_a$  is the value of the band gap with spin-orbit coupling ( $\Gamma_9^v \rightarrow \Gamma_7^c$ ) and  $\Delta$  is the value of the spin-orbit splitting. The spin-orbit coupling parameter  $\mu$  was chosen in order to satisfy this condition to better than 0.001 eV accuracy. For CdS crystal,  $\Delta = 0.062 \text{ eV}$  at 77K [43] and we determined that  $\mu = 0.00008$  is optimal. For CdSe crystal,  $\Delta = 0.42 \text{ eV}$  at 77 K [43] and we determined that  $\mu = 0.00041$  is optimal. Figure 1(a) show the band structure of a wurtzite CdS crystal, including the spin-orbit coupling. The discrete energy levels of a  $R = 15.0 \text{ \AA}$  zinc-blende CdS cluster, modelled as a sphere of radius  $R$ , are given in Fig. 1(b). Figure 1(c) show the band structure of a zinc-blende CdS crystal, compared with experimental data [44]. Figure 2(a) show the band structure of a wurtzite CdSe crystal, including the spin-orbit coupling, and 2(b) is the band structure of a zinc-blende CdSe crystal, compared with the available experimental data [44]. The study of the dependence of the excitonic energies on the cluster size was carried out using the bulk crystal parameters  $\epsilon = 5.5$ ,  $m_e = 0.19$ ,  $m_h = 0.80$  [30] for both wurtzite and zinc-blende CdS system, and  $\epsilon = 10.0$ ,  $m_e = 0.13$ ,  $m_h = 0.45$  [30] for both wurtzite and zinc-blende CdSe system. The exciton energies are reported in Tables IV–VII. Since for a cluster of radius  $R = 100 \text{ \AA}$  the fundamental gap is 2.46 eV for zinc-blende, and 2.55 eV for wurtzite, we shifted our conduction energy levels by +0.04 eV and -0.05 eV, respectively, in order to obtain the experimental bulk band gap of 2.50 eV. We carried out a similar correction of for CdSe clusters, shifting the conduction bands by -0.15 eV for zinc-blende, and -0.025 eV for wurtzite, so that we obtain the bulk band gap of 1.79 eV for a cluster of  $R = 100 \text{ \AA}$ . In Fig. 3 we compare the calculated exciton energies of both wurtzite and zinc-blende CdS clusters with the experimental data [28,45–48]. This figure clearly shows that the zinc-blende and wurtzite clusters exhibit different spectral shifts and the available experimental data follow one or the other of these trends. Based on these calculations, we can assign the zinc-blende structure to the clusters synthesized by Wang and Herron [47] and wurtzite structure to the smaller clusters synthesized by Weller and coworkers [48].

### 1. The Effect of Dielectric Constant and Spin-Orbit Coupling

We have investigated the dependence of the exciton energies on dielectric constant ( $\epsilon$ ) by carrying out calculations on CdSe clusters using two different values of  $\epsilon$ :  $\epsilon(0)$  and  $\epsilon(\infty)$ . Figure 4(a) compares the calculated exciton energies with the available experimental data [49–54]. The dashed line represents the calculations on wurtzite CdSe clusters with  $\epsilon(0) = 10.0$ , while the solid line represents the corresponding calculation with  $\epsilon(\infty) = 6.25$ . According to these results the exciton energies calculated with  $\epsilon(\infty)$  are closer to the experimental data. Figure 4(b) represents identical calculations on zinc-blende structure, with  $m_e = 0.11$  and  $m_h = 0.44$  [43], compared with the experiments [54–59]. In this case the exciton energies

seem to be insensitive to a reasonable choice of the dielectric constant.

The bulk wurtzite CdSe semiconductor exhibits three distinct transitions, labelled A, B, and C, arising from the splitting of the valence band due to spin-orbit interaction. If we assume that similar transitions will exist in clusters too, then we obtain the transitions shown in Fig. 4(c). Since the bulk transition A is at 1.79 eV [43], and that for a cluster of  $R = 100 \text{ \AA}$  is at 1.67 eV (using 233 plane waves), a correction of +0.12 eV was applied. The calculated transitions B and C were also similarly corrected: B bulk transition = 1.81 eV [43], cluster ( $R = 100 \text{ \AA}$ ) = 1.74 eV, so the correction = 0.07 eV; C bulk transition = 2.22 eV [43], cluster ( $R = 100 \text{ \AA}$ ) = 2.14 eV, so the correction = 0.08 eV. From Fig. 4(c) we observe that if only the lowest exciton energies are considered, then the experimental data show significant scatter compared to the calculated results. However, when we consider all three transitions (A, B, and C), then all the experimental data can be neatly accounted for as belonging to one of these three transitions. This finding indicates the possibility that some of the experimental data reported in the literature correspond to higher-energy transitions (B and C) rather than to the lowest energy transition A.

The spectroscopy of nanoscale CdSe clusters have attracted considerable attention from several research groups [49–54]. Some of these groups have succeeded in synthesizing CdSe cluster samples that have very narrow size distributions [51,53,54]. Furthermore, they have made very careful measurements of the exciton energies. For these reasons, direct comparison between our calculations and the data from these groups provides a benchmark test of the reliability of our computational method in yielding accurate exciton energies. From the results presented above it is clear that the agreement between our calculations and experiment is excellent. The experimental data lie much closer to our calculated values than to those of the EMM, without any exception. The experimental measurements on cluster samples with very narrow size distribution are in better agreement with our calculations than the corresponding data on samples with broad size distribution. Finally, we are able to identify that some measured exciton energies probably correspond to higher energy B and C transitions than to the lowest energy A transition.

## B. CdTe Clusters

Since both Cadmium and Tellurium are large atoms, the CdTe clusters and crystals exist only in zinc-blende form. Since both the cation and anion are heavy atoms, we expect significant spin-orbit coupling in CdTe. Consequently, we have carried out band structure calculations on zinc-blende CdTe clusters using non-local EPM with the effects of spin-orbit coupling included in the Hamiltonian [60]. The parameters used in these calculations are given in Tables II and III. The spin-orbit coupling parameter  $\mu$  was fit to the experimental band gap of 1.56 eV at 300 K [43].

Figure 5(a) presents the band structure for the zinc-blende CdTe crystal, while Fig. 5(b) compares the calculated direct exciton energies with the available experimental data [61,62]. In these calculations we used  $\epsilon = 10.2$ ,  $m_e = 0.09$ , and  $m_h = 0.72$  [43]. The exciton energies of spherical clusters of different radii are reported in Table VIII. The computational procedure employed is identical to that described above. At present, experimental data on CdTe clusters are few. However, we hope that our calculations will stimulate further experimental efforts on these clusters.

### C. AlP Clusters

The binary semiconductor AlP is isoelectronic to Si<sub>2</sub> and they both crystallize in an identical lattice structure. Also, since Al and P are the nearest neighbors of Si in the periodic table, it is reasonable to expect that crystalline AlP will have electronic properties similar to that of bulk Si. Indeed that turns out to be true: both Si and AlP are indirect gap semiconductors with similar band structures. Likewise, since both these semiconductors are made of light elements, we expect spin-orbit coupling to be negligible in these crystals. We have reported on our investigation of the spectral shifts of silicon clusters before. Now we present corresponding calculations on AlP clusters.

The previous calculated band structure of AlP was obtained using the LCAO-MO method and the corresponding band structure is not available from EPM calculations. Consequently, we have fitted the non-local parameters of AlP to reproduce the band structure calculated using the LCAO-MO method. Our initial guess for these parameters utilized the parameters of bulk Si [30]. In the end the optimal parameters gave 3.63 eV for the direct and 2.41 eV for the indirect gaps. These calculated values are in complete agreement with the corresponding experimental band gaps at 300 K [63]. Tables II and III give the parameters, while Fig. 6 gives the bulk band structure and the calculated exciton energies of AlP clusters. These calculations utilized  $\epsilon = 9.8$ ,  $m_e = 0.21$ , and  $m_h = 0.94$  [63,64]. The exciton energies are reported in Table IX. Nanoscale AlP clusters have not been synthesized in the laboratory so far. However, recent experimental efforts on Si clusters point to the possibility of similar interest on AlP clusters.

### D. GaP and GaAs clusters

Figures 7 and 8 give the band structures and the exciton energies of GaP and GaAs spherical clusters as a function of their radius. Tables II and III show the parameters that were used in these calculations [65]. Figures 7 (a) and 8 (a) show the band structures of zinc-blende GaP and GaAs crystals obtained using the non-local empirical pseudopotential (solid line) and the local empirical pseudopotential (dashed line). Comparison with the experimental data of GaP [66,67] and GaAs [66–69] crystals clearly shows that the non-local approximation yields to band structures that are better in agreement with the experimental data than those one obtained with the local approximation. Since GaP is an indirect gap semiconductor, we present spectral shifts of both the direct and indirect transitions. The results obtained from the use of both local and non-local EPM are shown in these figures. The calculated band gaps of GaP, obtained using 283 plane waves and the local EPM method, are 2.79 eV for the direct transition and 2.15 eV for the indirect transition. Since the corresponding experimental band gaps are 2.78 eV for the direct transition and 2.27 eV for the indirect transition [63], we shifted the calculated band gaps by -0.01 eV, and +0.12, respectively. The non-local EPM gives 2.88 eV and 2.17 eV, respectively, for the direct and the indirect band gaps of GaP. Consequently, the corresponding shifts are -0.10 eV and +0.10 eV.

For GaAs, the experimental direct gap is 1.47 eV, which is an average of the experimental band gaps at 0 and 300 K [63]. The calculated band gaps, obtained using 283 plane waves, are 1.50 eV with the local calculation and 1.52 eV with the non-local calculation. Consequently,

the corrections are -0.03 eV and -0.05 eV, respectively. We used the bulk crystal parameters  $\epsilon = 9.1$ ,  $m_e = 0.10$ ,  $m_h = 0.86$  [30] for GaP clusters, and  $\epsilon = 9.1$ ,  $m_e = 0.07$ ,  $m_h = 0.86$  [30] for GaAs clusters.

The exciton energies thus calculated are presented in Tables X–XII and Figs. 7 and 8. From these figures it is clear that over a large range of cluster sizes the local EPM is able to reproduce spectral shifts as accurately as non-local EPM for both GaP and GaAs. However, at small cluster sizes the non-local correction on the spectral shifts is significant. At large cluster sizes the absorption spectrum shifts to higher energies with decreasing cluster size. This blueshift is expected due to confinement of the electron-hole pair in the cluster. However, at small cluster sizes the absorption spectrum of GaAs clusters shifts to lower energies with decreasing cluster size; a trend opposite to that observed for large clusters. In the case of GaP, which is an indirect gap semiconductor, the lowest energy transition exhibits the expected blueshift at both large and small cluster sizes. But this transition is not observable because it is forbidden. The origin of the absorption spectrum, corresponding to the observable direct transition, shifts to lower energies with decreasing cluster size at small cluster sizes. Both local and non-local pseudopotentials exhibit the same qualitative behavior. The main difference is that the non-local EPM predicts less redshift in small clusters than the local EPM.

We can explain the calculated trends in the following way. At large cluster sizes the electron and hole are both confined in a spherical well. This quantum confinement increases the band gap with decreasing cluster size and it is the dominant effect in this size regime. In these large clusters, the negatively charged electron and the positively charged hole are spatially separated and hence the coulomb attraction between them is negligible. However, in small clusters the coulomb attraction energy between the electron-hole pair cannot be neglected. While the band gap still increases with decreasing cluster size, in small clusters this increase is sufficiently overcome by the coulomb energy that the spectra shift to lower energies. Consequently, in this small cluster size regime the absorption spectra of clusters may exhibit redshift instead of the blueshift.

At present reliable experimental data are not present for the spectral shifts of these important III-V semiconductor clusters, partly because of considerable experimental difficulties that arise in trying to synthesize III-V semiconductor clusters with narrow size distribution. However, based on our experience with CdS and CdSe clusters, and InP clusters (see below), we expect our calculated spectral shifts of AlP, GaP, and GaAs clusters to be good estimates of the expected spectral shifts.

## E. InP clusters

Recently, Nozik and co-workers have succeeded in synthesizing InP clusters and for the first time showed an exciton transition in the spectrum of a III-V quantum dot [70]. The present work compares their experimental results with our theoretical predictions. We used the same procedure as before: First, we found the parameters of the EPM Hamiltonian and then calculated the excitonic energies of InP clusters. The band structure calculations on zinc-blende InP crystal were carried out using the non-local EPM that includes the effects of spin-orbit coupling. The parameters we employ are slightly different from those used by Chelikowsky, but otherwise the two calculations give nearly identical band structures. In



particular, the coupling parameter  $\mu = 0.00023$  was chosen in order to reproduce the fundamental splitting = 1.50 eV, as obtained by Chelikowsky [60]. Complete set of parameters used in our calculations are tabulated in Tables II and III.

Figure 9(a) displays the band structure of bulk InP and Fig. 9(b) presents the exciton energies of the clusters as a function of their radius. These calculations have employed the parameters  $\epsilon = 9.61$ ,  $m_e = 0.077$ , and  $m_h = 0.58$  [63]. We shifted all the conduction bands by -0.207 eV so that the band gap of an  $R = 100$  Å cluster is equal to the experimental bulk value of 1.35 eV at 300 K. The exciton energies are reported in Table XIII.

The type (a) sample in the experiments of Nozik and co-workers have a radius of about 20 Å and exhibits an exciton transition at about 1.7 eV [70]. This paper quotes 0.35 eV blueshift for the onset of absorption for the colloidal sample (a) whose mean diameter is 26.1 Å. However, 0.35 eV is not the blueshift for a particle with a diameter of 26.1 Å because colloid (a) has a broad size distribution with a standard deviation of 7.5 Å (see Fig. 3 of Ref. [70]). Thus the onset of absorption really corresponds to a size of about 40 Å (private communication). We use this value for the particle size while comparing experimental blueshift with our calculations. The difference between our calculated exciton energy and the experimental value is approximately 0.17 eV. The type (c) sample has a radius of 13 Å and exciton transition at 2.25 eV, in perfect agreement with our calculation. From this comparison it is clear that the overall trend of the experimental spectral shifts is in close agreement with our calculations. Additional reliable data on spectral shifts over a range of cluster sizes will certainly be useful in establishing the accuracy of our calculations.

Our band structure calculations on all IIIA-VB semiconductor clusters have shown that local empirical pseudopotentials are reasonably accurate compared to the non-local empirical pseudopotentials for the calculations of the spectral shifts of these clusters. The non-local corrections on the spectral shifts are most important in small cluster sizes. In addition, our calculations have shown that, while quantum confinement energy is the dominant factor affecting spectral shifts in large clusters, the Coulomb interaction between the electron and hole has significant effect in small clusters. The attractive Coulomb interaction is sufficiently strong in small clusters that it overcomes the confinement energy of the electron-hole pair and gives rise to redshift, instead of the blueshift, of the electronic absorption spectrum.

## VI. SUMMARY

In summary, we calculated the spectral shifts of CdS, CdSe, CdTe, AlP, GaP, GaAs, and InP semiconductor clusters using the most accurate available empirical pseudopotentials. These semiconductors cover a wide range of bond polarities and band structures. These binary clusters also represent a series in which one ion is held constant while the other ion is varied along a column of the periodic table. Furthermore, the pseudopotentials employed in these calculations incorporate the effects of non-locality and spin-orbit coupling whenever they are important. For many of these semiconductors, we had to first determine the pseudopotential parameters based on the latest experimental and theoretical data. Consequently, we report complete set of pseudopotential parameters employed in our calculations. Furthermore, we also give full details of our band structure calculations employing pseudopotentials that incorporate both non-local and spin-orbit effects. At present these calculations represent the most sophisticated calculations on the spectral shifts of semiconductor clusters.

Previously we had shown that a simple local pseudopotential yields spectral shifts of zinc-blende CdS clusters in excellent agreement with experiment over a range of cluster sizes. Now we extend these calculations to include the effects of spin-orbit coupling in the pseudopotential. As before, we find that for zinc-blende CdS, wurtzite CdS, wurtzite CdSe, and zinc-blende InP clusters the spectral shifts calculated using our band structure model are in excellent agreement with experiment. The shapes and crystal structures of the unit cell have significant effect on the exciton energies. The small clusters in particular are sensitive to whether their crystal structure is zinc-blende or wurtzite. In the case of small CdS clusters where the experimental data on lattice structure are either ambiguous or unavailable, our calculations are able to assign the structure unambiguously. While reliable experimental data are not yet available at present for zinc-blende CdSe clusters, we predict that the spectral shifts in these clusters will be nearly the same as those of wurtzite clusters.

In the absence of experimental data on CdTe, AlP, GaP, and GaAs clusters, our calculations provide reasonable estimates of the expected spectral shifts and trends in these clusters as a function of cluster size. The very little difference between the local and the non-local calculations confirms the validity of the local pseudopotential method for the calculations of the exciton energies. The main effect of the non-local pseudopotentials seems to be to reduce the magnitude of the redshift seen in the spectral shifts of some small III-V semiconductor clusters. Similarly, the spin-orbit interaction does not change the lowest exciton energies. The main effect of the spin-orbit interaction is to split the valence band into subbands, thus giving rise to new transitions in the spectra. Some experimental data seem to be in better agreement with these higher energy transitions, thus suggesting the possibility that transitions originating from spin-orbit split valence bands are being observed even in these nanoscale clusters. This also conceivably explains the reasons for considerable scatter in the experimentally determined exciton energies for a given cluster size. This study, together with our previous investigation, provides evidence that the empirical pseudopotential method yields unique insights into the quantum confinement effects and is a powerful tool for calculating the spectral shifts of semiconductor clusters.

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# TABLES

TABLE I. Reciprocal lattice vectors and form factors (in a.u.) for CdS and CdSe crystals.

$\mathbf{G}$	$G^2$	CdS		CdSe	
		$V_S$	$V_A$	$V_S$	$V_A$
Zinc-blende					
000	0	0.000	0.000	0.000	0.000
111	3	-0.120	0.115	-0.115	0.095
200	4	0.000	0.065	0.000	0.060
220	8	0.015	0.000	0.005	0.000
311	11	0.020	0.025	0.020	0.025
222	12	0.000	0.025	0.000	0.025
400	16	0.000	0.000	0.000	0.000
Wurtzite					
000	0	0.000	0.000	0.000	0.000
001	$\frac{3}{4}$	0.000	0.000	0.000	0.000
100	$2\frac{2}{3}$	-0.130	0.000	-0.125	0.000
002	3	-0.120	0.115	-0.115	0.095
101	$3\frac{3}{12}$	-0.100	0.090	-0.100	0.075
102	$5\frac{2}{3}$	-0.015	0.040	-0.035	0.045
003	$6\frac{3}{4}$	0.000	0.000	0.000	0.000
210	8	0.015	0.000	0.005	0.000
211	$8\frac{3}{4}$	0.000	0.000	0.000	0.000
103	$9\frac{5}{12}$	0.020	0.025	0.015	0.025
200	$10\frac{2}{3}$	0.020	0.000	0.020	0.000
212	11	0.020	0.025	0.020	0.025
201	$11\frac{5}{12}$	0.020	0.025	0.020	0.025
004	12	0.000	0.025	0.000	0.025
202	$13\frac{2}{3}$	0.010	0.015	0.010	0.015
104	$14\frac{2}{3}$	0.000	0.010	0.000	0.010
213	$14\frac{3}{4}$	0.000	0.000	0.000	0.000

TABLE II. The Pseudopotential parameters of the semiconductors. The parameters  $V_S$ ,  $V_A$ ,  $\alpha_0$ , and  $A_2$  are in a.u.,  $a_0$  is in Å, and  $\beta_0$  and  $\mu$  are dimensionless.

Compound	$V_S(\sqrt{3})$	$V_S(\sqrt{8})$	$V_S(\sqrt{11})$	$V_A(\sqrt{3})$	$V_A(\sqrt{4})$	$V_A(\sqrt{11})$	$a_0$ (Å)
Local parameters							
CdTe	-0.11000	0.00000	0.03100	0.03000	0.02500	0.01250	6.48
AlP	-0.12250	0.01000	0.02000	0.05000	0.03000	0.00005	5.46
GaP	-0.11500	0.01000	0.02900	0.05000	0.03500	0.01300	5.45
GaAs	-0.10700	0.00700	0.03900	0.02800	0.01900	0.00100	5.65
InP	-0.11750	0.00000	0.02650	0.04000	0.03000	0.01500	5.86
Non-local parameters							
	Cation			Anion			Spin Orbit
	$\alpha_0$	$\beta_0$	$A_2$	$\alpha_0$	$\beta_0$	$A_2$	$\mu$
CdS	...	...	...	...	...	...	0.00008
CdSe	...	...	...	...	...	...	0.00041
CdTe	0.000	0.400	0.000	0.000	0.400	1.000	0.00061
AlP	0.190	0.300	0.350	0.160	0.030	0.180	...
GaP	0.000	0.300	0.200	0.160	0.050	0.225	...
GaAs	0.000	0.000	0.063	0.000	0.000	0.313	...
InP	0.000	0.250	0.275	0.150	0.050	0.175	0.00023

TABLE III. The Pseudopotential parameters  $R_0$  and  $R_2$  in Å.

Compound	Cation		Anion	
	$R_0$	$R_2$	$R_0$	$R_2$
CdTe	1.37	1.41	1.06	1.41
AlP	1.06	1.19	1.06	1.19
GaP	1.27	1.19	1.06	1.19
GaAs	1.27	1.44	1.06	1.44
InP	1.27	1.29	1.06	1.29

TABLE IV. Band gaps and exciton energies of zinc-blende CdS spherical clusters obtained using 283 plane waves.  $R$  is the radius of the cluster,  $k$  is the angular momentum wave vector of the lowest exciton state,  $E_g$  is the band gap,  $V_c$  is the Coulomb energy, and  $E_x$  is the exciton energy.

$R(\text{\AA})$	$k(2\pi/a_0) = a_0/\sqrt{12}R$	$E_g$ (eV)	$V_c$ (eV)	$E_x$ (eV)
5.0	0.3359	4.69	-0.93	3.77
10.0	0.1680	3.69	-0.46	3.24
15.0	0.1120	3.14	-0.31	2.85
30.0	0.0560	2.65	-0.15	2.51
50.0	0.0336	2.52	-0.09	2.44
99.0	0.0170	2.46	-0.04	2.43

TABLE V. Band gaps and exciton energies of wurtzite CdS spherical clusters obtained using 233 plane waves and neglecting the spin-orbit coupling.  $R$  is the radius of the cluster,  $k$  is the angular momentum wave vector of the lowest exciton state,  $E_g$  is the band gap,  $V_c$  is the Coulomb energy, and  $E_x$  is the exciton energy.

$R(\text{\AA})$	$k(\sqrt{2}\pi/a_0) = a_0/\sqrt{6}R$	$E_g$ (eV)	$V_c$ (eV)	$E_x$ (eV)
5.0	0.337700	5.66	-0.93	4.66
10.0	0.1689	3.92	-0.46	3.39
15.0	0.1126	3.27	-0.31	2.89
30.0	0.0563	2.74	-0.15	2.52
50.0	0.0338	2.60	-0.09	2.45
99.0	0.0171	2.54	-0.04	2.43

TABLE VI. Band gaps and exciton energies of zinc-blende CdSe spherical clusters obtained using 283 plane waves.  $R$  is the radius of the cluster,  $k$  is the angular momentum wave vector of the lowest exciton state,  $E_g$  is the band gap,  $V_c$  is the Coulomb energy, and  $E_x$  is the exciton energy.

$R(\text{\AA})$	$k(2\pi/a_0) = a_0/\sqrt{12}R$	$E_g$ (eV)	$V_c$ (eV)	$E_x$ (eV)
5.0	0.351000	4.18	-0.51	3.51
10.0	0.1755	3.18	-0.25	2.77
15.0	0.1170	2.64	-0.17	2.31
30.0	0.0585	2.14	-0.08	1.90
50.0	0.0351	2.00	-0.05	1.79
99.0	0.0177	1.94	-0.02	1.76



TABLE VII. Band gaps and exciton energies of wurtzite CdSe spherical clusters obtained using 233 plane waves and neglecting the spin-orbit coupling.  $R$  is the radius of the cluster,  $k$  is the angular momentum wave vector of the lowest exciton state,  $E_g$  is the band gap,  $V_c$  is the Coulomb energy, and  $E_x$  is the exciton energy.

$R(\text{\AA})$	$k(\sqrt{2}\pi/a_0) = a_0/\sqrt{6}R$	$E_g$ (eV)	$V_c$ (eV)	$E_x$ (eV)
5.0	0.3510	5.00	-0.51	4.45
10.0	0.1755	3.28	-0.25	3.00
15.0	0.1170	2.60	-0.17	2.40
30.0	0.0585	2.04	-0.08	1.92
50.0	0.0351	1.88	-0.05	1.80
99.0	0.0177	1.81	-0.02	1.76

TABLE VIII. Band gaps and exciton energies of zinc-blende CdTe spherical clusters obtained using 137 plane waves and including the spin-orbit coupling.  $R$  is the radius of the cluster,  $k$  is the angular momentum wave vector of the lowest exciton state,  $E_g$  is the band gap,  $V_c$  is the Coulomb energy, and  $E_x$  is the exciton energy.

$R(\text{\AA})$	$k(2\pi/a_0) = a_0/\sqrt{12}R$	$E_g$ (eV)	$V_c$ (eV)	$E_x$ (eV)
5.0	0.3741	3.40	-0.50	2.89
10.0	0.1871	3.00	-0.25	2.75
15.0	0.1247	2.53	-0.16	2.36
30.0	0.0624	1.94	-0.08	1.86
50.0	0.0374	1.75	-0.05	1.69
99.0	0.0189	1.65	-0.02	1.62

TABLE IX. Band gaps and exciton energies of zinc-blende AlP spherical clusters obtained using 283 plane waves.  $R$  is the radius of the cluster,  $k$  is the angular momentum wave vector of the lowest exciton state,  $E_{xd}$  is the direct exciton energy, and  $E_{xi}$  is the indirect exciton energy.

$R(\text{\AA})$	$k(2\pi/a_0) = a_0/\sqrt{12}R$	$E_{xd}$ (eV)	$E_{xi}$ (eV)
5.0	0.3154	3.91	3.83
10.0	0.1577	4.02	2.93
15.0	0.1051	3.97	2.68
30.0	0.0526	3.73	2.46
50.0	0.0315	3.63	2.41
99.0	0.0159	3.58	2.39

TABLE X. Band gaps and exciton energies of zinc-blende GaP spherical clusters obtained using 283 plane waves and the local pseudopotential.  $R$  is the radius of the cluster,  $k$  is the angular momentum wave vector of the lowest exciton state,  $E_{xd}$  is the exciton energy for the direct transitions, and  $E_{xi}$  is the exciton energy for the indirect transitions.

$R(\text{\AA})$	$k(2\pi/a_0) = a_0/\sqrt{12}R$	$E_{xd}$ (eV)	$E_{xi}$ (eV)
6.0	0.2624	3.09	3.15
12.0	0.1312	3.43	2.58
18.0	0.0875	3.25	2.43
30.0	0.0525	2.99	2.31
51.0	0.0309	2.84	2.26
99.0	0.0159	2.79	2.25

TABLE XI. Band gaps and exciton energies of zinc-blende GaP spherical clusters obtained using 283 plane waves and the non-local pseudopotential.  $R$  is the radius of the cluster,  $k$  is the angular momentum wave vector of the lowest exciton state,  $E_{xd}$  is the exciton energy for the direct transitions, and  $E_{xi}$  is the exciton energy for the indirect transitions.

$R(\text{\AA})$	$k(2\pi/a_0) = a_0/\sqrt{12}R$	$E_{xd}$ (eV)	$E_{xi}$ (eV)
6.0	0.2624	3.50	3.36
12.0	0.1312	3.57	2.67
18.0	0.0875	3.33	2.49
30.0	0.0525	3.05	2.36
52.0	0.0303	2.89	2.31
98.0	0.0152	2.84	2.30

TABLE XII. Band gaps and exciton energies of zinc-blende GaAs spherical clusters obtained using 283 plane waves.  $R$  is the radius of the cluster,  $k$  is the angular momentum wave vector of the lowest exciton state,  $E_{xl}$  is the exciton energy for the direct transitions in a local calculation, and  $E_{xnl}$  is the direct exciton energy in a non-local calculation.

$R(\text{\AA})$	$k(2\pi/a_0) = a_0/\sqrt{12}R$	$E_{xl}$ (eV)	$E_{xnl}$ (eV)
6.0	0.2718	2.29	2.42
12.0	0.1359	2.45	2.40
18.0	0.0906	2.14	2.11
30.0	0.0544	1.76	1.75
51.0	0.0320	1.54	1.54
99.0	0.0165	1.44	1.44

TABLE XIII. Band gaps and exciton energies of zinc-blende InP spherical clusters obtained using 137 plane waves and including the spin-orbit coupling.  $R$  is the radius of the cluster,  $k$  is the angular momentum wave vector of the lowest exciton state,  $E_g$  is the band gap,  $V_c$  is the Coulomb energy, and  $E_x$  is the exciton energy.

$R(\text{\AA})$	$k(2\pi/a_0) = a_0/\sqrt{12}R$	$E_g$ (eV)	$V_c$ (eV)	$E_x$ (eV)
5.0	0.3384	3.12	-0.53	2.37
10.0	0.1692	2.89	-0.26	2.42
15.0	0.1128	2.50	-0.17	2.12
30.0	0.0564	1.90	-0.08	1.60
50.0	0.0338	1.67	-0.05	1.41
99.0	0.0171	1.55	-0.02	1.32

## FIGURES

FIG. 1. a) Band structure of a wurtzite CdS crystal implementing the spin-orbit interactions and 135 plane waves. b) Allowed electronic levels of wurtzite CdS spherical clusters (radius = 15 Å) obtained using 233 plane waves. c) Band structure of a zinc-blende CdS crystal obtained using 283 plane waves. Experimental data are superimposed on the band structure for comparison [44].

FIG. 2. a) Band structure of a wurtzite CdSe crystal implementing the spin-orbit interactions and 135 plane waves. b) Band structure of a zinc-blende CdSe crystal obtained using 283 plane waves. Experimental data are superimposed on the band structure for comparison [44].

FIG. 3. Direct exciton energy of wurtzite (upper line), and zinc-blende (lower line) CdS spherical clusters compared with the experiments. Filled diamonds are used for the zinc-blende data points while filled circles represent the wurtzite clusters. 233 plane waves were used for the wurtzite and 283 plane waves for the zinc-blende structures.

FIG. 4. a) Direct exciton energies of wurtzite CdSe clusters obtained using two different dielectric constants:  $\epsilon(0)$  (dashed line), and  $\epsilon(\infty)$  (solid line). Comparison is made with the available experimental data: stars [49]; plus [50]; squares [51]; up triangles (light-hole data from [52]); down triangles (split-off-hole data from [52]); diamonds [53]; circles (SAXS data from [54]); right triangles (TEM data from [54]). b) Direct exciton energies of zinc-blende CdSe clusters obtained using two different dielectric constant:  $\epsilon(0)$  (dashed line), and  $\epsilon(\infty)$  (solid line). The comparison is made with the available experimental data: up triangles (SAXS data from [54]); down triangles (TEM data from [54]); circles [55]; squares [56]; star [57]; plus [58]; diamonds [59]. c) Calculated A (lower line), B (intermediate line), C (upper line) transition energies, as discussed in the text. The experimental data are represented as in (a).

FIG. 5. a) Band structure of zinc-blende CdTe crystals obtained using 137 plane waves and the spin-orbit interactions. b) Direct exciton energies of zinc-blende CdTe clusters compared with the experiments: circles [61]; diamonds [62].

FIG. 6. a) Band structure of a zinc-blende AlP crystal obtained using 283 plane waves. b) Direct exciton energies of zinc-blende AlP clusters obtained using 283 plane waves. c) Indirect exciton energies of zinc-blende AlP clusters obtained using 283 plane waves.

FIG. 7. a) Band structure of a zinc-blende GaP crystal obtained using 283 plane waves.. It is shown a comparison between the non-local (solid line) and the local (dashed line) empirical approximation. Experimental data are superimposed on the band structure: diamonds [66]; plus symbols [67]. The non-local pseudopotential calculations are seen to agree better with the experimental data than the local pseudopotential calculations. b) Direct exciton energies of zinc-blende GaP clusters. The open circles are obtained using local pseudopotentials and filled circles are obtained using non-local pseudopotentials. c) Indirect exciton energies of zinc-blende GaP clusters. The open circles are obtained using local pseudopotentials and filled circles are obtained using non-local pseudopotentials.

FIG. 8. a) Band Structure of a zinc-blende GaAs crystal. It is made a comparison between the non-local (solid line), and the local (dashed line) empirical approximation. Experimental data are superimposed on the band structure: diamonds [66]; plus symbols [67];  $\times$  symbols [68]; squares [69]. The non-local pseudopotential calculations agree better with the experimental data than the local calculations. b) Direct exciton energies of GaAs spherical clusters. The open circles are obtained using local pseudopotentials and filled circles are obtained using non-local pseudopotentials. The number of plane waves used is 283.

FIG. 9. a) Band structure of a zinc-blende InP crystal obtained using 137 plane waves and spin-orbit interactions. b) Direct exciton energies of zinc-blende InP clusters compared with experiments: circles [70].